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Technical Report 32-1188

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Abstract

The technique of hot isostatic pressing was used to fabricate solid magnesium oxide, MgO, bodies of high purity with respect to metallic impurities to 90% to 95% density, with high translucency, and having a grain size of approximately 0.2 μ. The densified material contained significant amounts of brucite, $Mg(OH)_2$, as a result of the presence of water which was in the starting material and was not removed during vacuum baking. The fabricated pieces showed large numbers of cracks which were apparently introduced into the compacts prior to densification.

When the hot-pressed pieces were reheated, the brucite decomposed, the density increased and the porosity coalesced while grain growth occurred. The general technique appears to be usable for the fabrication of finely divided powders if improvements are made in powder degassing and predensification procedures.

Fabrication and Characterization of Hot Isostatically Pressed MgO

I. Introduction

A relatively recent addition to the fabrication techniques available for use with ceramics is hot isostatic pressing (Ref. 1). This technique is expected to offer a considerable advantage by producing fine-grain, high-density ceramic bodies which should be extremely strong; and its lower pressing temperature should reduce contamination. However, little evidence in the literature has been noted on the use of the technique or the evaluation of the product (Ref. 2).

Hot isostatic pressing is considered here as a means of producing magnesium oxide blanks which could be machined into conventional tensile specimens. The preparation of these blanks generated considerable information concerning the structure and chemistry of the product, and is reported here. Samples were also characterized after being reheated.

II. Materials and Procedure

The types of magnesium oxide powders used in this study are described in Table 1. They were isostatically pressed[1] to 90,000 psi at room temperature, in rubber

[1]The hot isostatic pressing and associated preparation were conducted by Battelle Memorial Institute, Columbus, Ohio.

Table 1. MgO powders for hot isostatic pressing

Sample	Type	Particle size, Å	Density after cold-compacted, g/cc	Remarks
1	JPL[a]	126	2.00	Some radial cracks
2	JPL	146	2.14	
3	JPL	155	2.10	Some radial cracks
4	JPL	248	1.97	
5	Fisher M-300	225	2.04	
6	Fisher M-300	225	1.98	
7	Baker *Heavy*	NA[b]	2.51	
8	Baker *Heavy*	NA	2.47	
9	Fisher M-300	225	2.03	
10	Fisher M-300	225	2.01	
11	Baker *Light*	NA	2.00	Circumferential cracks
12	JPL	166	NA	Containers leaked during cold compaction. Discarded
13	JPL	177	NA	

[a]See Reference 3.
[b]Not available.

bags, and attained a theoretical density of approximately 55%. These blanks were then handshaped with abrasive paper to fit the metal jackets for subsequent hot compaction. The jackets were cleaned with a 30% nitric acid solution and rinsed with alcohol before being loaded with the compacts. The compacts were outgassed, in place, through a ¼-in. vacuum stem for four hours at 250°C at a vacuum of 40 μ. They were cooled under vacuum conditions and sealed by crimping. Hot isostatic compaction was then performed at 15,000 psi for thirty

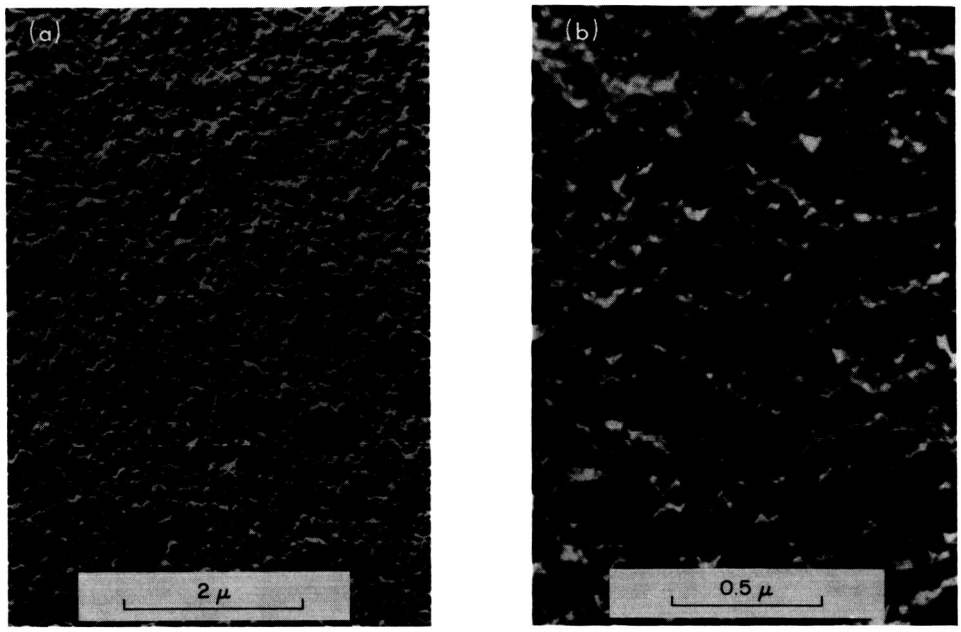

Fig. 1. Electron micrograph of replica of hot isostatically pressed MgO after steam etch of replica: (a) Sample 1, (b) Sample 2 (micrograph courtesy of Sloan Research Industries, Santa Barbara, Calif.)

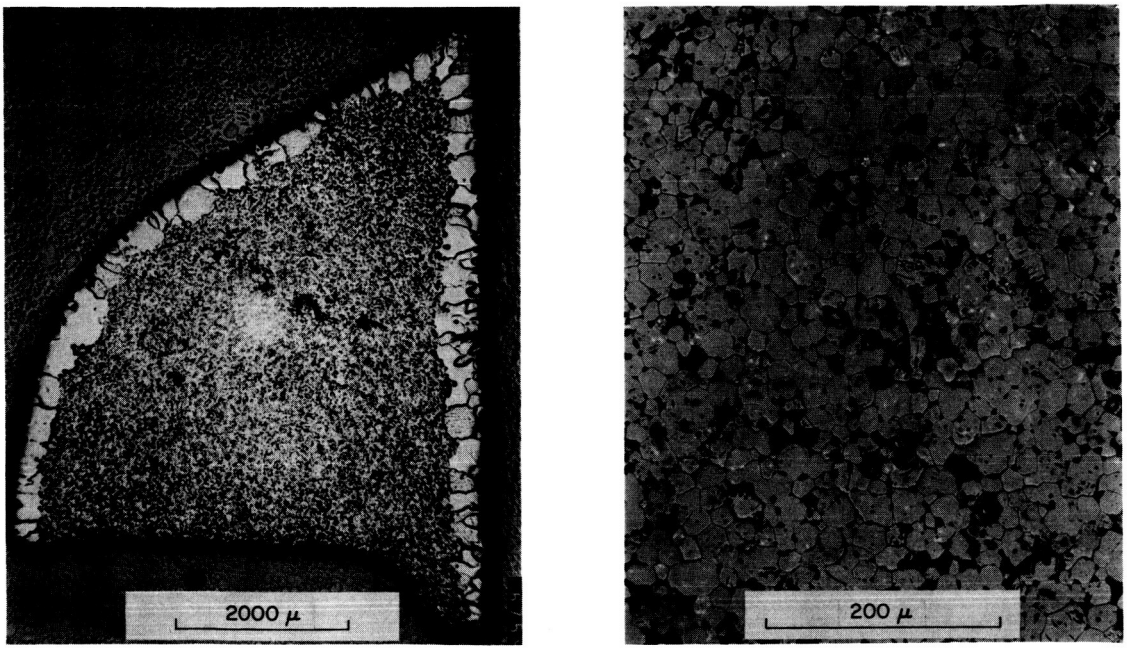

Fig. 2. Sample 3 of hot isostatically pressed MgO after reheating to 1750°C

Table 2. MgO compacts after hot isostatic pressing

Sample	Density, g/cc	Grain size, μ	Unit cell, Å	$Mg(OH)_2$ present	Jacket material	Remarks
1	2.99	0.1	ND[a]	ND	Mild steel	White, fine longitudinal cracks, severely etched, thin reaction layer with container, glassy, translucent.
2	3.11	0.15	4.2132	Slight		White, severe longitudinal cracks, severely etched, thin reaction layer with container, glassy, translucent, specimen intact.
3	3.15	0.15	4.2133	Slight		White, fine longitudinal cracks, severely etched, thin reaction layer with container, glassy, translucent.
4	3.33	0.3	4.2134	Slight		White with light-blue tint, severely etched, thin reaction layer with container, glassy, severe longitudinal cracking, translucent.
5	2.1	0.05	ND	ND		White, severely cracked, porous.
6	NA[b]	NA	4.2133	Yes	Mild steel	White, severely cracked, porous.
7	NA	NA	NA	ND	304 SS	White, fine hairline cracks, glassy, appears translucent.
8	3.30	ND	ND	ND	Mild steel	Cream color, bluish discoloration, slightly etched, glassy, no apparent cracking.
9	—	—	—	—	304 SS	Container leaked, specimen not densified.
10	—	—	—	—	304 SS	Container leaked, specimen not densified.
11[c]	3.27	ND	ND	ND	Mild steel	Light cream color, several longitudinal cracks intact, glassy, slightly etched.

[a]Not determined.
[b]Not available.
[c]ZrO_2 barrier layer used to prevent jacket reaction.

minutes at 800°C with approximately linear rates of pressure and maximum values of temperature. The total heating and cooling cycle, including the hold, lasted approximately five hours. The maximum conditions were selected from experience with uniaxial pressing of these powders (Ref. 3) so as to produce 95% to 98% of theoretical density. The jackets were then removed by acid leaching in 30% HNO_3.

III. Results

Eight finished compacts were obtained and examined for such characteristics as appearance, lattice spacing, apparent specific gravity, weight loss, chemistry and microstructure. Microstructures are shown in Figs. 1 and 2. The reheated specimens were placed in magnesium oxide muffles and heated in air, then re-examined. The observed data are summarized in Tables 2, 3, and 4. The properties determined were evaluated by standard techniques which are more thoroughly described in previous reports (Refs. 4, 5). Because of the superior density and available history of the starting powders produced at the Jet Propulsion Laboratory (JPL), the bulk of the analysis was conducted on these specimens.

Table 3. Effect of heat treatment in air on hot isostatically pressed MgO

Sample	Reheat 1 h, °C	Density, g/cc	Grain size, μ	Lattice parameter, Å	Brucite present	Percent weight loss (from as-pressed condition)
2	None	3.11	0.10	4.2132	Slight	—
3	None	3.15	0.15	4.2133	Slight	—
4	None	3.33	0.30	4.2134	Slight	—
2	1010	ND[a]	<1[b]	4.2132	None	3.2
3	1010	3.32	<1[b]	4.3132		3.0
4	1010	ND	<1[b]	4.2132		1.8
2	1750	3.32	40/500[c]	4.2131		3.1
3	1750	3.38	50/500[c]	4.2131		3.1
4	1750	3.42	40/1000	4.2132	None	1.7

[a]Not determined.
[b]Not optically resolved.
[c]Duplex structure. See Figure 2.

Table 4. Mass spectrographic analysis of Sample 3 of MgO

Element	Symbol	Powder, ppm at.	Hot isostatically pressed		
			As-pressed, ppm at.	Reheated at 1010°C, ppm at.	Reheated to 1750°C, ppm at.
Hydrogen	H	100,000[a]	30,000	5,000	1,000
Hydroxyl	OH[b]	30,000[a]	3,000	300	100
Lithium	Li	0.5	0.3	0.3	≤1
Boron	B	≤0.1	10	25	≤1
Carbon	C	5,000[a]	2,000	1,000	1,000
Nitrogen	N	300[a]	300	100	50
Fluorine	F	<1	10	20	1
Sodium	Na	<1	10	<1	<1
Aluminum	Al	30	10	3	20
Silicon	Si	<3	100	100	400
Phosphorus	P	0.3	5	3	2
Sulfur	S	10	100	100	100
Chlorine	Cl	40	100	12	40
Potassium	K	10	30	≤1	10
Calcium	Ca	30	20	10	50
Titanium	Ti	<10	<4	<1	40
Chromium	Cr	0.2	1	4	10
Manganese	Mn	0.3	≤0.3	1	10
Iron	Fe	3	10	10	100
Cobalt	Co	<0.1	1	<0.1	1
Nickel	Ni	≤0.2	1	1	15
Copper	Cu	1	15	15	15
Zinc	Zn	5	10	10	15
Lead	Pb	<0.2	1	3	1

[a]Sample not baked. Others baked 150°C, 12 h, in source.
[b]Read at m/e 17.

IV. Discussion

It was immediately evident upon examination of the finished compacts that further development would be required to produce structurally sound specimen blanks. Cracking, which was largely longitudinal, showed in all the pieces, although some of this cracking had appeared in the cold-pressed compacts. Because many of the cracks showed contamination from iron deposits, it is believed that such cracks occurred before densification. Apparently pressure was sufficient to collapse the jacket and to crack the soft compacts during heating. It is in this area—preparation, handling, and cold compaction prior to densification—that major development is required. The compaction parameters themselves appear to be less troublesome.

Failure to obtain crack-free specimens prevented the measurement of such properties as mechanical strength or thermal conductivity. Evaluation was limited to that reported on microstructure and chemistry.

Tables 2 and 3 show that at a temperature of 800°C some grain growth occurred during the compaction of the JPL powder. Subsequent reheating to higher temperatures resulted in normal grain growth. The duplex structure shown in Fig. 2 is undoubtedly related to the loss of pores by outward diffusion that removed this source of grain growth inhibitors. The effect is accentuated by the lack of normal impurities at the grain boundaries, in this material, to act as further inhibitors.

The mass spectrographic analysis shown in Table 4 indicates that pieces can be produced by this technique which are nearly free from metallic impurities. The increase in some levels of these impurities during the 1750°C reheat is not typical; in any event, such behavior is unrelated to the fabrication.

The levels of anionic impurities, even after the reheating of the specimen, again indicate the stability of such impurities (Refs. 3, 5, 6) in magnesium oxide. However, the loss of considerable amounts of two of these impurities, hydrogen and carbon, is indicated by both the weight changes given in Table 3 and the chemical analysis in Table 4. The state of the large amount of hydrogen in the as-pressed magnesium oxide was brucite, noted by the presence of additional lines in the x-ray patterns. In Samples 2, 3, and 4 the amount was estimated at 5% by weight brucite in the magnesium oxide. No evidence of these lines showed in the samples reheated to 1010°C or 1750°C. If the weight loss (3.1%) in Sample 3 is assumed to be brucite decomposition, the 10% by weight brucite in the original sample is indicated, probably a more accurate value. The chemical analysis value 3.3% atomic weight (H + OH) would appear low since this amount would produce only 2.4% by weight brucite; but, considering the approximate nature of these analyses, this must be considered reasonable agreement.

The final pressing conditions of 15,000 psi and 800°C were above the equilibrium decomposition temperature of brucite (Refs. 7, 8) at 15,000 psi. The fact that brucite was still present in the samples may be due either to the

material not attaining equilibrium or to the reformation of brucite during the cooling cycle. The latter is likely since fine-grained reactive magnesium oxide can transform into brucite after a short reaction time and since the fabrication process used here favored the periclase + water → brucite transformation during most of the cooling cycle.

The carbon loss (as CO_2) from the chemical analysis accounts for only 0.2% weight loss and no evidence of any carbonate-bearing phases was observed in the x-ray patterns.

The presence of the significant amounts of hydrogen in the reheated specimens is more difficult to explain in terms of brucite since the temperatures are well above the decomposition temperature of 350°C. Some mechanism involving high pressures and lack of exit paths might be invoked to explain stability of hydrogen as brucite at 1010°C but at 1750°C, with 10% porosity, this is difficult to accept. It seems more reasonable to propose the stability of hydroxyl in magnesium oxide either as complexes (Ref. 9) or at interfaces (Ref. 6). Infrared transmission studies do show the presence of such bonds in polycrystalline magnesium oxide[2] (Ref. 10); however, such studies are not yet available in detail. Further, lack of sufficient total transmission in many samples of polycrystalline magnesium oxide limits the ultimate sensitivity of infrared for these bonds.

The densities obtained with these hot isostatic pressings were somewhat lower than was expected (85% to 90% compared with an expected 95% to 98%) apparently because the problem of the gaseous impurities was underestimated. For example, inclusion of 10% brucite in specimen 3 lowers the theoretical density to 3.41% and raises the relative density of the actual compact to 92.5%. Porosity must account for the remaining volume, with entrapped gases possibly stabilizing the void volume. In spite of the presence of porosity, the high translucency of the as-pressed compacts and the 1010°C reheated specimens suggests that the light-scattering centers are far smaller than the wavelengths of light. This is supported by average grain sizes of 0.09–0.3 μ.

[2]Personal communication from A. T. Chapman, Georgia Institute of Technology, May 1966.

V. Conclusions

Several conclusions were drawn from this study.

(1) Hot isostatic pressing is effective in densifying very fine-grained magnesium oxide at temperatures and pressures which may be reasonably predicted from uniaxial pressing.

(2) Care must be taken to avoid fracture of compacts due to deformation of the container before densification, since such fractures do not heal.

(3) Improved techniques are needed for properly removing gaseous materials from the cold-compacted powders without reducing sinterability.

(4) Gaseous impurities may remain as stable additional compounds after exposure to temperatures far above their decomposition temperature during fabrication or reheat, or both.

(5) After the highest reheat treatment (1750°C), such compounds are below the limit of detection by x-ray diffraction; however, such gaseous species remain as the principal impurity in a 90% dense body.

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